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(54) Title: PREPARATION OF OXIRANE COMPOUNDS

(57) Abstract: Process for the preparation of oxirane compounds, which process comprises: (i) oxidation of an alkylaryl to obtain an alkylaryl hydroperoxide, (ii) contacting at least part of the alkylaryl hydroperoxide obtained in step (i) with olefin in the presence of a catalyst to obtain an oxirane compound and alkylaryl hydroxyl, (iii) optionally reacting at least part of the alkylaryl hydroperoxide obtained in step (i) to obtain phenol and a ketone, (iv) separating oxirane compound from reaction product of step (ii), and (v) contacting at least part of the reaction product from which an oxirane compound has been separated, with hydrogen in the presence of a hydrogenation catalyst to obtain alkylaryl at least part of which is recycled to step (i).

## PREPARATION OF OXIRANE COMPOUNDS

The present invention relates to a process for the preparation of oxirane compounds.

Processes for preparing oxirane compounds such as propylene oxide, have been known for a long time.

5 US-A-3,350,422 describes a method comprising reacting olefinically unsaturated compounds, preferably propylene, with an organic hydroperoxide in the presence of an effective dissolved catalytic amount of a soluble vanadium compound. It is described that during the  
10 epoxidation reaction the organic hydroperoxide is converted almost quantitatively to the corresponding alcohol. The alcohol can be recovered as co-product, or reconverted to the hydroperoxide by dehydration to olefin, hydrogenation of the olefin, and oxidation to  
15 hydroperoxide, or by hydrogenolysis to hydrocarbon followed by oxidation to hydroperoxide.

NL-C-1010372 describes a process comprising reacting propene with ethylbenzene hydroperoxide to obtain propylene oxide and 1-phenyl ethanol. The 1-phenyl  
20 ethanol is subsequently dehydrated to obtain styrene, which is a useful starting material for other chemical reactions. NL-C-1012749 describes a similar process in which propene is reacted with cumenehydroperoxide to obtain propene oxide and 2-phenyl-2-propanol. The latter  
25 is described to be subsequently dehydrated into alpha-methylstyrene which is described to be an industrially applicable compound.

Suitable outlets can often be found for many of the products co-produced in the prior art processes for  
30 manufacturing oxirane compounds. However, it can be

beneficial to be able to produce solely the oxirane compound such as propylene oxide.

5 In EP-B-609455, a process is described for producing cresol by (1) oxidation of cymene to obtain a solution of oxygenation products containing tertiary hydroperoxide and primary hydroperoxide, (2) reduction of the content of primary hydroperoxide, (3) decomposition of the reaction mixture to obtain cresol and some by-products, and (4) subjecting the decomposition mixture to  
10 hydrogenation to convert part of the by-products to cymene and/or cresol. EP-B-609455 solely relates to the preparation of cresol.

A process has now been found which makes it possible to prepare oxirane compounds without the need to prepare  
15 further compounds at the same time. Although some of the process steps of the process according to the present invention are known per se, there is no teaching or hint in the prior art to combine these process steps in this particular way.

20 The present invention relates to a process for the preparation of oxirane compounds, which process comprises:

- (i) oxidation of an alkylaryl to obtain an alkylaryl hydroperoxide,
- 25 (ii) contacting at least part of the alkylaryl hydroperoxide obtained in step (i) with olefin in the presence of a catalyst to obtain an oxirane compound and alkylaryl hydroxyl,
- (iii) optionally reacting at least part of the alkylaryl hydroperoxide obtained in step (i) to obtain phenol and a  
30 ketone,
- (iv) separating oxirane compound from reaction product of step (ii),
- (v) contacting at least part of the reaction product  
35 from which the oxirane compound has been separated, with

hydrogen in the presence of a hydrogenation catalyst, to obtain alkylaryl at least part of which is recycled to step (i).

5 US-A-3,350,422 mentions that an alcohol can be reconverted to its hydroperoxide by dehydration to olefin, hydrogenation of the olefin, and oxidation to hydroperoxide, or by hydrogenolysis to hydrocarbon followed by oxidation to hydroperoxide. However, US-A-3,350,422 contains no specific information on how an  
10 alcohol can be reconverted to its hydroperoxide in a technically and commercially attractive way.

It has now surprisingly been found that in the process of the present invention, the alkylaryl hydroxide can be converted into the alkylaryl with the help of  
15 hydrogen and in the presence of a hydrogenation catalyst. In many cases undesired by-products which were formed in a previous step, were converted into the desired alkylaryl as well. The latter is attractive in that it increases the overall yield of the process.

20 Although ethylbenzene is the alkylaryl compound most widely used in the preparation of an oxirane compound at present, it has been found that process step (i) can be carried out at higher conversion and higher selectivity if the alkylaryl compound employed is an alkylbenzene in  
25 which the alkyl substituent is a branched alkyl substituent comprising from 3 to 10 carbon atoms. A more preferred alkylaryl compound contains 1 or 2 alkyl substituents. An alkylaryl compound containing several substituents has the advantage that it can contain  
30 several hydroperoxide groups. However, in view of potential side-reactions, it is preferred that there are no more than 3 substituents, more preferably no more than 2 substituents. Most preferably, the alkylaryl compound is cumene and/or di(iso-propyl)benzene. Although mixtures  
35 of different alkylaryl compounds can be employed, a

single type of compound is preferred in order to be able to optimise the process conditions for this specific compound.

5 The oxidation of the alkylaryl can be carried out by any suitable process known in the art. The oxidation can be carried out in the liquid phase in the presence of a diluent. This diluent is preferably a compound which is liquid under the reaction conditions and does not react with the starting materials and product obtained.

10 However, the diluent can also be a compound necessarily present during the reaction. For example, if the alkylaryl is cumene the diluent can be cumene as well.

15 The product obtained in step (i) can be used as such in step (ii), or it can be preferred to separate off some compounds, or it can be preferred to only use part of the product obtained and to use another part in another process.

20 Preferably, part of the product of step (i) is used in step (iii), namely reaction of the alkylaryl hydroperoxide to obtain phenol and ketone. The phenol obtained can contain substituents. The reaction of the alkylaryl hydroperoxide can be attained by contacting the alkylaryl hydroperoxide with an acidic catalyst such as acidic catalysts containing sulphur. As the acidic catalyst can  
25 be used sulphuric acid, hydrochloric acid, perchloric acid, sulphur dioxide and sulphur trioxide; organic acids such as benzenesulphonic acid, p-toluenesulphonic acid, cresolsulphonic acid and chloroacetic acid; solid acids such as silica-alumina, alumina and acidic ion exchange  
30 resins; heteropolyacids such as tungstosilicic acid, tungstophosphoric acid and molybdophosphoric acid. Preferably, sulphuric acid and/or cresolsulphonic acid are used. The amount of catalyst to be used is usually in the range of from 0.0001 to 1 %wt, based on the reaction

mixture to be treated. The reaction temperature is usually in the range of from 30 to 150 °C.

The alkylaryl can be subjected to the reaction after other compounds have been separated off from the reaction product of step (i). However, it is preferred to subject part of the reaction product of step (i) directly to the decomposition reaction of step (iii).

The reaction in step (iii) usually produces by-products. By-products which are frequently found, are ethylbenzene and 1-methyl styrene. In order to further increase the yield of the present process, the desired products phenol and ketone can be separated from the reaction product of step (iii), after which either all or part of the remaining reaction product is subjected to the hydrogenation of step (v). Therefore, the process according to the present invention preferably comprises separating at least part of the phenol and ketone from the reaction product of step (iii), and contacting either all or part of the remaining reaction product with hydrogen in step (v). Compounds which are obtained in step (iii) and which are preferably sent to step (v) are ethylbenzene and 1-methyl styrene. Therefore, any fraction of the reaction product of step (iii) which is sent to step (v) preferably contains ethylbenzene and/or 1-methyl styrene. Reaction product of step (iii) can be sent to step (v) as such, or the reaction product of step (iii) is combined with reaction product of step (iv) from which oxirane compound has been separated off, before being sent to step (v).

The desired phenol and ketone can be separated from the reaction product of step (iii) in any way known to someone skilled in the art. Preferably, the phenol and ketone are substantially removed from the reaction product of step (iii), while at least part of the

reaction products other than phenol and ketone is sent back to the integrated process.

If part of the alkylaryl hydroperoxide is converted into phenol and ketone, it is preferred that the alkylaryl is cumene as this gives phenol and acetone in step (iii).

In step (ii), alkylaryl hydroperoxide obtained in step (i) is contacted with olefin in the presence of a catalyst to obtain an oxirane compound and hydroxy-alkylaryl. A catalyst which can suitably be used in such process comprises titanium on silica and/or silicate. A preferred catalyst is described in EP-B-345856. Such catalyst comprises titanium in chemical combination with a solid silica and/or inorganic silicalite which catalyst is obtainable by a) impregnating the silicium compound with a stream of gaseous titanium tetrachloride, b) calcining the obtained reaction product of step a) and c) hydrolysis of the product of step b). The reaction generally proceeds at moderate temperatures and pressures, in particular at temperatures in the range of from 0 to 200 °C, preferably in the range from 25 to 200 °C. The precise pressure is not critical as long as it suffices to maintain the reaction mixture in a liquid condition. Atmospheric pressure may be satisfactory. In general, pressures can be in the range of from 1 to  $100 \times 10^5 \text{ N/m}^2$ .

The olefin to be used in the process in the present invention depends on the oxirane compound to be prepared. Preferably, the olefin contains from 2 to 10 carbon atoms, more preferably from 2 to 8 carbon atoms. Most preferably, the olefin is propene.

At the conclusion of the epoxidation reaction, the liquid mixture comprising the desired products is separated from the catalyst. The oxirane compound can then be separated from the reaction product in any way

known to be suitable to someone skilled in the art. The liquid reaction product may be worked up by fractional distillation, selective extraction and/or filtration. The catalyst, any solvent which might be present and any unreacted olefin or alkylaryl hydroperoxide may be recycled for further utilization.

Process step (ii) can be carried out with the catalyst in the form of a slurry, of a moving bed or a fluidized bed. However, a fixed bed is preferred for large-scale industrial application. The process may be carried out in a batch-wise manner, semi-continuously or continuously. The liquid containing the reactants may then be passed through the catalyst bed, so that the effluent from the reaction zone is substantially free from catalyst.

Subsequently, at least part of the reaction product containing hydroxyalkylaryl from which an oxirane compound has been separated off, is subjected to hydrogenation. A hydrogenation treatment which can be used comprises contacting reaction product with hydrogen at a temperature of from 100 to 330 °C, preferably of from 140 to 330 °C, preferably of from 180 to 330 °C, preferably of from 180 to 320 °C, and a pressure of from 0.1 to  $100 \times 10^5 \text{ N/m}^2$ , more preferably of from 0.1 to  $50 \times 10^5 \text{ N/m}^2$ , most preferably of from 0.1 to  $30 \times 10^5 \text{ N/m}^2$ . The ratio (mol/mol) of hydrogen to alkylaryl hydroxide contacted with the catalyst is preferably at least 0.5, more preferably at least 1.0, most preferably at least 1.4. The hydrogenation treatment is carried out in the presence of a hydrogenation catalyst. Generally, the hydrogenation catalyst will contain a metal on a solid carrier which metal catalyses hydrogenation. Preferred catalysts are catalysts containing from 0.5 to 5 %wt of metal or a metal compound on a carrier. Preferably, the metal present as metal or

metal compound is one or more metal chosen from Group 1b, 2b, 3a, 4a, 4b, 5b, 6b, 7b and 8 of the Periodic Table of the Elements described in the Handbook of Chemistry and Physics, 63rd Edition. Most preferably, the metal present as metal or metal compound is palladium. It was found that such catalysts can give a high conversion.

Catalysts suitable for use in hydrogenating at least part of the reaction product containing hydroxyalkylaryl from which an oxirane compound has been separated off, are the catalysts described in US 5,475,159. These catalysts are catalysts comprising a copper compound, a zinc compound and at least one compound selected from the group consisting of aluminium, zirconium, magnesium, a rare earth and mixtures thereof. Such catalysts were found to give good results at relatively low temperature. In step (v) of the present process, these catalysts are preferably used at a temperature of from 100 to 250 °C. Preferably, such catalysts comprise from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of copper. Further, such catalysts preferably contain from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of zinc. A preferred catalyst contains from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of copper, from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of zinc, and from about 0.1 percent by weight to about 20 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of rare earth. A further preferred catalyst contains from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of copper, from

about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of zinc, and from about 0.05 percent by weight to about 30 percent by weight, basis the total weight of the catalyst, of aluminium. A further preferred catalyst contains from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of copper, from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of zinc, and from about 0.05 percent by weight to about 30 percent by weight, basis the total weight of the catalyst, of zirconium. Another preferred catalyst contains from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of copper, from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of zinc, from about 0.05 percent by weight to about 30 percent by weight, basis the total weight of the catalyst, of zirconium, and from about 0.05 percent by weight to about 30 percent by weight, basis the total weight of the catalyst, of aluminium. And a further preferred catalyst contains from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of copper, from about 10 percent by weight to about 80 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of zinc, from about 0.05 percent by weight to about 30 percent by weight, basis the total weight of the catalyst, of magnesium, and from about 0.1 percent by weight to about 20 percent by weight, calculated as the oxide, basis the total weight of the catalyst, of rare earth.

After hydrogenation, the hydrogenated product can be recycled in toto or in part. If only part of the hydrogenated product is recycled, the desired fraction can be separated off in any way known to be suitable to someone skilled in the art.

The process according to the present invention is illustrated by the following Examples.

Example 1

The epoxidation catalyst was a catalyst containing titanium on silica which was prepared as described in the Example according to the teaching of EP-A-345856.

The hydrogenation catalyst was a catalyst containing copper, zinc and zirconium prepared according to Example 3 of US-A-5,475,159.

Fresh cumene and recycled cumene are fed to a reactor. During 8 hours, air is bubbled in at the bottom of the reactor and leaves at the top of the reactor. The reactor is cooled during the reaction. The reaction product obtained contained 28 %wt of cumene hydroperoxide, 70 %wt of cumene and 2 %wt of further compounds.

A reaction mixture containing about 6 mol of 1-octene per mol of cumene hydroperoxide was fed to a reactor containing the fresh epoxidation catalyst described above at a temperature of 40 °C. Octene oxide was separated off. It was found that 55 %wt of 1-octene was converted into octene oxide.

A mixture containing 17%wt of 2-phenyl-2-propanol and 83 %wt of cumene was contacted with hydrogen in the presence of the hydrogenation catalyst described above at a temperature of 140 °C and a pressure of  $20 \times 10^5$  N/m<sup>2</sup> during 2 hours. The product obtained contained no i-propylcyclohexane, 86 %wt of cumene, 10 %wt of 2-phenyl-2-propanol and 4 %wt of 1-methyl styrene.

Example 2

A mixture containing 17 %wt of 2-phenyl-2-propanol and 83 %wt of cumene was contacted with hydrogen in the presence of a hydrogenation catalyst comprising 5 %wt of palladium on a charcoal carrier, at a temperature of 225 °C and a pressure of  $20 \times 10^5$  N/m<sup>2</sup> during 2 hours. The product obtained contained 1 %wt of 2-phenyl-2-propanol, 94 %wt of cumene, 3 %wt of i-propylcyclohexane and 2 %wt of further compounds.

Example 3

The experiment of Example 2 was repeated with the difference that the temperature was 280 °C. The product obtained contained no 2-phenyl-2-propanol, 89 %wt of cumene, 10 %wt of i-propylcyclohexane and 1 %wt of further compounds.

Example 4

Fresh ethylbenzene and recycled ethylbenzene are fed to a reactor. During 8 hours, air is bubbled in at the bottom of the reactor and leaves at the top of the reactor. The reactor is cooled during the reaction due to the exothermic nature of the oxidation. The reaction product obtained contained 10 %wt of ethyl benzene hydroperoxide, 88 %wt of ethylbenzene and 2 %wt of further compounds.

A reaction mixture containing about 6 mol of 1-octene per mol of ethylbenzene hydroperoxide was fed to a reactor containing the fresh epoxidation catalyst described in Example 1 at a temperature of 40 °C. Octene oxide was separated off. It was found that 41 %wt of 1-octene was converted into octene oxide.

Example 5

The feed used in Examples 5-7 had the following composition:

cumene	74.7%
1-methyl styrene	0.8%
2-phenyl-2-propanol	24.5%

5 The feed contained no heavy compounds containing at least 10 carbon atoms (C10+ material), based on analysis by gas chromatography.

The hydrogenation catalyst was a catalyst as used in Example 1 containing copper, zinc and zirconium prepared according to Example 3 of US-A-5,475,159.

10 A fixed bed of the hydrogenation catalyst was contacted with the feed at a weight hourly space velocity (WHSV) of  $1.0 \text{ hr}^{-1}$  (33.64 g of feed per hour), a reactor bed temperature of  $200^\circ\text{C}$ , a reactor operating pressure of  $20 \times 10^5 \text{ N/m}^2$  and 0.8 mole of hydrogen per mole of  
15 2-phenyl-2-propanol fed. A product of the following composition was obtained:

cumene	93.1%
1-methyl styrene	0.7%
2-phenyl-2-propanol	5.9%
20 C10+ material	0.3%

#### Example 6

Example 5 was repeated except that the amount of hydrogen was 1.6 mole of hydrogen per mole of 2-phenyl-2-propanol fed. The further reaction conditions were a  
25 weight hourly space velocity (WHSV) of  $1.0 \text{ hr}^{-1}$  (33.64 g of feed per hour), a reactor bed temperature of  $200^\circ\text{C}$ , and a reactor operating pressure of  $20 \times 10^5 \text{ N/m}^2$ . The product obtained had the following composition:

cumene	97.3%
30 1-methyl styrene	0.3%
2-phenyl-2-propanol	0.1%
C10+ material	2.3%

Example 7

Example 6 was repeated except that the temperature of the reactor bed was increased to 220 °C. The further reaction conditions were a hydrogen flow rate of 1.6 mole  
5 of hydrogen per mole of 2-phenyl-2-propanol fed, a WHSV of 1.0 hr<sup>-1</sup> (33.64 g of feed per hour), and a reactor operating pressure of 20 x 10<sup>5</sup> N/m<sup>2</sup>. The product obtained had the following composition:

	cumene	97.8%
10	1-methyl styrene	0.0%
	2-phenyl-2-propanol	0.0%
	C10+ material	2.2%

C L A I M S

1. Process for the preparation of oxirane compounds,  
which process comprises:
- (i) oxidation of an alkylaryl to obtain an alkylaryl  
hydroperoxide,
  - 5 (ii) contacting at least part of the alkylaryl hydro-  
peroxide obtained in step (i) with olefin in the presence  
of a catalyst to obtain an oxirane compound and alkylaryl  
hydroxyl,
  - (iii) optionally reacting at least part of the alkylaryl  
10 hydroperoxide obtained in step (i) to obtain phenol and a  
ketone,
  - (iv) separating oxirane compound from reaction product  
of step (ii), and
  - (v) contacting at least part of the reaction product  
15 from which an oxirane compound has been separated, with  
hydrogen in the presence of a hydrogenation catalyst to  
obtain alkylaryl at least part of which is recycled to  
step (i).
2. Process according to claim 1, in which process the  
20 alkylaryl compound is an alkylbenzene in which the alkyl  
substituent is a branched alkyl substituent comprising  
from 3 to 10 carbon atoms.
3. Process according to claim 1 or 2, in which process  
the alkylaryl compound is cumene and/or di(iso-  
25 propyl)benzene.
4. Process according to any one of claims 1 to 3, in  
which at least part of the phenol and ketone are  
separated from the reaction product of step (iii), and  
either all or part of the remaining reaction product is  
30 contacted with hydrogen in step (v).

5. Process according to any one of claims 1 to 4, in which in step (ii) alkylaryl hydroperoxide is contacted with propene at a temperature in the range of from 0 to 200 °C, and a pressure in the range of from 1 to 5 100 x 10<sup>5</sup> N/m<sup>2</sup> in the presence of a catalyst comprising titanium on silica and/or silicate.

6. Process according to any one of claims 1 to 5, in which the hydrogenation of in process step (v) is carried out at a temperature of from 100 to 330 °C, and a 10 pressure of from 0.1 to 50 x 10<sup>5</sup> N/m<sup>2</sup>.

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(54) Title: PROCESS FOR PREPARING OXIRANE COMPOUNDS

(57) Abstract: Process for the preparation of oxirane compounds, which process comprises: (i) oxidation of an alkylaryl to obtain an alkylaryl hydroperoxide, (ii) contacting at least part of the alkylaryl hydroperoxide obtained in step (i) with olefin in the presence of a catalyst to obtain an oxirane compound and alkylaryl hydroxyl, (iii) optionally reacting at least part of the alkylaryl hydroperoxide obtained in step (i) to obtain phenol and a ketone, (iv) separating oxirane compound from reaction product of step (ii), and (v) contacting at least part of the reaction product from which an oxirane compound has been separated, with hydrogen in the presence of a hydrogenation catalyst to obtain alkylaryl at least part of which is recycled to step (i).



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## INTERNATIONAL SEARCH REPORT

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 A. CLASSIFICATION OF SUBJECT MATTER  
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 345 856 A (SHELL INT RESEARCH) 13 December 1989 (1989-12-13) cited in the application page 1, line 1 -page 2, line 53 claim 1	1-6
Y	EP 0 361 755 A (MITSUI PETROCHEMICAL IND) 4 April 1990 (1990-04-04) cited in the application example 1 claim 1	1-6
Y	US 6 160 137 A (ISHINO MASARU ET AL) 12 December 2000 (2000-12-12) cited in the application example 1 claim 1	1-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Inter. Application No.

PCT/EP 01/14750

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